

# Kinetic models for polyatomic molecules with phenomenological energy exchange

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Models of the collision integral are developed for polyatomic structureless molecules subject to certain classes of phenomenological energy exchange between internal and translational energy modes in binary collisions. The exchange is described either by a model differential cross section for energy scattering or equivalently by a set of pair pseudo-internal coordinates which correlate pre- and post-collision values of the particle energies. Restrictions placed on admissible models of the exchange process are identified and one recently proposed special model is reformulated under these conditions. Chapman-Enskog type transport properties for this model are evaluated and its behavior in the context of the Monte-Carlo direct simulation method is discussed briefly.

## I. INTRODUCTION

The kinetic theory of neutral polyatomic molecules (i.e., those with internal energy) is very complicated largely because of the complex processes by which molecules may exchange active internal and translational energy in inelastic collisions. While polyatomic kinetic equations for the dilute classical,<sup>1</sup> semi-classical,<sup>2</sup> and fully quantum-mechanical (Ref. 3, Chap. 11) gas are available, the formidable task of solving the binary inelastic collision problem required by the theory has severely limited their practical application.

For the calculation of highly nonequilibrium flow fields of a monatomic gas, one method that has been widely applied is Bird's<sup>4</sup> direct simulation Monte-Carlo method, in which the full classical nonlinear Boltzmann equation is simulated directly on a digital computer, by the calculated motion, including collisions, of several thousand sample particles taken to represent the distribution function. For the monatomic case, the elastic collision problem is straightforward and general spherical potential models such as inverse power (Ref. 3, p. 239) molecules are readily incorporated into the Bird simulator.

Efforts to extend the direct simulation method to polyatomic gases have focused largely on the relatively simple case of a rotationally active diatomic gas. Impulsive classical collision models have been successfully tested by Bird<sup>5</sup> (rough spheres) and Melville<sup>6</sup> (loaded spheres), but they are perhaps too artificial for use in general simulation studies. Macpherson<sup>7</sup> has adapted Parker's<sup>8</sup> more realistic classical soft potential rigid roter model for strong normal shock wave simulations, calculating the complete molecular trajectories for each collision. Although exact, this is a very time consuming procedure that is presently out of the question for the treatment of complex flows.

Models based on approximate solutions to the inelastic collision problem have been developed by several authors. The present author<sup>9</sup> has utilized a solution to the Parker model by classical perturbation methods, as a basis for a hybrid classical/phenomenological description of the exchange process. While good results were

obtained with this scheme in several applications,<sup>10,11</sup> it was found that due to violation of detailed balancing, a result of the large number of approximations used in the analysis, the Boltzmann distribution of rotational energy at equilibrium was not obtained. This problem has been largely overcome by Deiwert and Yoshikawa<sup>12</sup> and Yoshikawa and Itakawa<sup>13</sup> who utilize approximate solutions for a semi-classical model of rotational transition probabilities in inelastic collisions. However, reported execution times for these models appear to limit their general application at present.

Models in which the effects of internal degrees of freedom operate simply as a phenomenological internal-translational energy exchange superimposed upon the otherwise monatomic collision dynamics have been proposed by Borgnakke and Larsen,<sup>14,15</sup> Bird,<sup>16</sup> and Koura.<sup>17</sup> This approach is based on the assumption that for determining the macroscopic flow properties, the finer details of the collision process may be ignored. While this leads to a problem much simpler than that of the direction solution of the inelastic collision dynamics, the nontrivial difficulty still remains of constructing a model which properly satisfies detailed balancing. Koura's model for discrete internal states satisfies this condition as does the "statistical" model of Borgnakke and Larsen.<sup>14</sup> Their<sup>15</sup> restricted exchange model based, on the concept of local equilibrium at the particle pair level, between partial degrees of freedom active during collision formally violates detailed balancing but with small error. This last scheme has been successfully employed by the present author in blunt body transition flow simulations.<sup>18</sup>

The relative simplicity and flexibility of the phenomenological approach suggests that its generalization along lines similar to the analogous theory for gas-surface interactions<sup>19</sup> may be worthwhile and this is one aim of the present paper. We consider a "kinetic theory" for structureless polyatomic molecules subject to a general class of phenomenological internal-translational energy exchange in binary collisions. Firstly, information theory principles are used to develop a contracted description of the gas in terms of a reduced distribution function  $f$ . A kinetic equation is obtained for  $f$ , and then

a simpler model kinetic equation is proposed by analogy, in which the energy exchange may be modeled heuristically. As examples of special models the restricted exchange scheme of Ref. 15 is modified into a form consistent with the present theory, and expressions for transport properties are evaluated as a means of determining disposable parameters. Finally, the behavior of these models in Monte-Carlo simulations is briefly discussed.

While the present theory was developed with specific reference to the direct simulation method, there seems no reason why it could not be treated by other standard kinetic theory techniques such as the various moment-expansion methods.

## II. MODEL KINETIC EQUATIONS

We shall consider a contracted description of the gas in which the dependence of the distribution function on the internal co-ordinates of the molecules reduces to dependence on the internal energy alone. The microscopic state of the gas is thus to be described by the distribution function  $f(\mathbf{c}, \epsilon, \mathbf{x}, t)$  with the usual meaning where  $t$ ,  $\mathbf{x}$ ,  $\mathbf{c}$ , and  $\epsilon$  are the time, position vector, particle velocity, and particle internal energy, respectively. Before developing our model kinetic equations we first obtain the appropriate entropy functional for our contracted description and relate  $f$  to the generalized single particle distribution function.

### A. The entropy functional

Let each of  $q_i$ ,  $i=1, \nu$  be either a generalized internal co-ordinate or momenta for a single particle, and assume that some canonical transformation can be found for which the single particle Hamiltonian is

$$\mathcal{H} = \frac{1}{2} m c^2 + \sum_{i=1}^{\nu} a_i q_i^2. \quad (1)$$

The summed term in Eq. (1) is then just  $\epsilon$  with  $\nu$  internal degrees of freedom. Let  $F(\mathbf{c}, \mathbf{q})$  be the generalized single particle distribution function in  $(\mathbf{c}, \mathbf{q})$  space where  $\mathbf{q} = (q_1, \dots, q_\nu)$ . The entropy is then

$$S = - \int \cdots \int F(\mathbf{c}, \mathbf{q}) \ln[F(\mathbf{c}, \mathbf{q})] d\mathbf{c} d\mathbf{q}. \quad (2)$$

To facilitate the transition from an  $F$  description to an  $f$  description, we introduce the transformation

$$\epsilon = \sum_{i=1}^{\nu} a_i q_i^2, \quad z_j = a_j q_j^2 / \sum_{i=1}^{\nu} a_i q_i^2, \quad j=2 \dots \nu \quad (3)$$

which will conveniently allow separate treatment of  $\epsilon$ . The Jacobian of Eqs. (3) is

$$J = \frac{\partial(q_1, \dots, q_\nu)}{\partial(\epsilon, z_2, \dots, z_\nu)} = K \epsilon^{\nu/2-1} G(\mathbf{z}), \quad (4)$$

where,

$$G(\mathbf{z}) = \prod_{j=2}^{\nu} \beta \left\langle z_j \left| \frac{1}{2}, \frac{j-1}{2} \right\rangle, \quad (5)$$

$$\beta \langle z | \mu_1, \mu_2 \rangle = \frac{1}{B(\mu_1, \mu_2)} z^{\mu_1-1} (1-z)^{\mu_2-1}, \quad (6)$$

$B(\mu_1, \mu_2)$  is the complete beta function and  $K$  is a constant.

The normalized distribution function in  $(\mathbf{c}, \epsilon; \mathbf{z})$  space is

$$F_{\mathbf{z}}(\mathbf{c}, \epsilon; \mathbf{z}) = J F(\mathbf{c}, \mathbf{q}) \quad (7)$$

while under Eqs. (3), Eq. (2) becomes

$$S = \int \int S_{\mathbf{z}}(\mathbf{c}, \epsilon) d\mathbf{c} d\epsilon \quad (8)$$

$$S_{\mathbf{z}} = - \int_0^1 \int_0^1 \cdots \int_0^1 F_{\mathbf{z}} \ln(F_{\mathbf{z}}/J) d\mathbf{z}, \quad (9)$$

where  $S_{\mathbf{z}}$  is the partial entropy with  $d\mathbf{z} = dz_2 dz_3 \dots dz_\nu$ . Our reduced distribution function is

$$f(\mathbf{c}, \epsilon) = \int_0^1 \int_0^1 \cdots \int_0^1 F_{\mathbf{z}}(\mathbf{c}, \epsilon; \mathbf{z}) d\mathbf{z}. \quad (10)$$

If we have no information regarding the distribution of  $\mathbf{z}$ , that is, we know  $f$  but not  $F_{\mathbf{z}}$ , then interpreting  $S_{\mathbf{z}}$  in Eq. (9) as Shannon's<sup>20</sup> measure of uncertainty or "randomness" for  $F_{\mathbf{z}}$ , the most unbiased estimate of  $F_{\mathbf{z}}$  may be obtained by maximizing  $S_{\mathbf{z}}$  subject to the constraint Eq. (10). We thus choose  $F_{\mathbf{z}}$  to be the most random possible distribution consistent with knowledge of  $f(\mathbf{c}, \epsilon)$ . This may be achieved using the standard variational method of Lagrange multipliers,<sup>20</sup> the results for  $S_{\mathbf{z}}$ ,  $F_{\mathbf{z}}$  being

$$S_{\mathbf{z}} = -f(\mathbf{c}, \epsilon) \{ \ln[f(\mathbf{c}, \epsilon)/\epsilon^{\nu/2-1}] - \ln(K) \} \quad (11)$$

$$F_{\mathbf{z}} = f(\mathbf{c}, \epsilon) G(\mathbf{z}). \quad (12)$$

Substituting Eq. (11) into Eq. (8), and Eq. (12) into Eq. (7) and using Eq. (4), we obtain, respectively, the best estimates of  $S$  and  $F$  with knowledge only of  $f$ , viz.,

$$S = - \int \int f(\mathbf{c}, \epsilon) \ln[f(\mathbf{c}, \epsilon)/\epsilon^{\nu/2-1}] d\mathbf{c} d\epsilon + \text{const}, \quad (13)$$

$$F = (1/K) f(\mathbf{c}, \epsilon) / \epsilon^{\nu/2-1}. \quad (14)$$

### B. Equation for $f(\mathbf{c}, \epsilon)$

Chapman and Cowling<sup>1</sup> obtain the generalized Boltzmann equation for  $F$ . For an elemental volume  $d\mathbf{c}_1 d\mathbf{q}_1 d\mathbf{x}$  of the  $(6+\nu)$  dimensional phase space of particle 1, in the absence of external forces, this may be written as

$$\left( \frac{\partial(nF_1)}{\partial t} + \mathbf{c}_1 \cdot \frac{\partial(nF_1)}{\partial \mathbf{x}} + \dot{\mathbf{q}}_1 \cdot \frac{\partial(nF_1)}{\partial \mathbf{q}_1} \right) d\mathbf{c}_1 d\mathbf{q}_1 d\mathbf{x} = L(f, f) d\mathbf{c}_1 d\mathbf{q}_1 d\mathbf{x}, \quad (15)$$

where

$$L(f, f) = n^2 \int \cdots \int (F'_1 F'_2 - F_1 F_2) g \hat{\sigma} d\mathbf{e}' d\mathbf{c}_2 d\mathbf{q}_2, \quad (16)$$

is the collision integral representing the gain into  $d\mathbf{c}_1 d\mathbf{q}_1 d\mathbf{x}$  due to collisions with particles labeled 2,  $\hat{\sigma} = \hat{\sigma}(g, \mathbf{q}_1, \mathbf{q}_2, \chi, \theta)$  is the cross section for scattering into  $d\mathbf{e}' = \sin \chi d\chi d\theta$  and the other quantities have the usual meaning. In Eq. (16) the two-particle Liouville theorem<sup>1</sup>

$$g \hat{\sigma} d\mathbf{e}' d\mathbf{c}_1 d\mathbf{c}_2 d\mathbf{q}_1 d\mathbf{q}_2 = g' \hat{\sigma}' d\mathbf{e} d\mathbf{c}'_1 d\mathbf{c}'_2 d\mathbf{q}'_1 d\mathbf{q}'_2 \quad (17)$$

has been utilized (the primed quantities refer to the post collision set), but the existence of inverse collisions has not been assumed.

Substituting Eq. (14) into Eqs. (15) and (16), utilizing Eqs. (3) and (4), dividing by  $dc_1 d\epsilon_1 d\mathbf{x}$  and integrating the resultant equation over all  $z_{1j}$ ,  $j=2 \dots \nu$  in  $(0, 1)$  yields an equation for  $f(\mathbf{c}, \epsilon)$

$$\frac{\partial(nf_1)}{\partial t} + \mathbf{c}_1 \cdot \frac{\partial(nf_1)}{\partial \mathbf{x}} = Q(f, f), \quad (18)$$

where

$$Q(f, f) = n^2 \int \dots \int [f'_1 f'_2 \mathcal{J} - f_1 f_2] g \hat{\sigma} d\mathbf{e}' d\mathbf{c}_2 d\epsilon_2 d\mathbf{Z}, \quad (19)$$

$\mathcal{J} = (\epsilon_1 \epsilon_2 / \epsilon'_1 \epsilon'_2)^{\zeta-1}$  with  $\zeta = \nu/2$  and  $d\mathbf{Z} = G(\mathbf{z}_1)G(\mathbf{z}_2) d\mathbf{z}_1 d\mathbf{z}_2$ . The internal energy term on the left-hand side has vanished due to

$$\dot{\mathbf{q}}_1 \cdot \frac{\partial(nF_1)}{\partial \mathbf{q}_1} = \frac{\partial(nF_1)}{\partial \epsilon_1} \frac{d\epsilon_1}{dt} = 0$$

since  $\epsilon$  is constant between collisions. Using Eqs. (3) and (4) in Eq. (17) together with  $dc_1 dc_2 = d\mathbf{w} g^2 dg d\mathbf{e}$ , where  $\mathbf{w} = (\mathbf{c}_1 + \mathbf{c}_2)/2$  leads to

$$\hat{\sigma} g^3 dg \epsilon_1^{\zeta-1} \epsilon_2^{\zeta-1} d\epsilon_1 d\epsilon_2 d\mathbf{Z} = \hat{\sigma}' g'^3 dg' \epsilon_1'^{\zeta-1} \epsilon_2'^{\zeta-1} d\epsilon_1' d\epsilon_2' d\mathbf{Z}'. \quad (20)$$

Equation (19) may be rewritten by putting

$$I(\epsilon|\epsilon') d\epsilon' = \int \int_{\Gamma} \hat{\sigma} d\mathbf{Z}, \quad I(\epsilon|\epsilon) d\epsilon = \int \int_{\Gamma'} \hat{\sigma}' d\mathbf{Z}', \quad (21)$$

where  $\epsilon = (\epsilon_1, \epsilon_2, \epsilon_t)$ ,  $\epsilon_t = mg^2/4$  is the relative translational energy in the pair mass center, and  $d\epsilon = d\epsilon_1 d\epsilon_2 d\epsilon_t$ .  $I(\epsilon|\epsilon') d\epsilon'$ , a function of the polar deflection angles  $(\chi, \theta)$  is the probability for energy transition into  $d\epsilon'$  and scattering into  $d\mathbf{e}'$ .  $\Sigma$  is the projection onto  $\mathbf{z}_1, \mathbf{z}_2$  space of a volume  $\Gamma$  of two-particle phase space and  $\Sigma'$  is the projection of  $\Gamma'$  onto  $\mathbf{z}_1', \mathbf{z}_2'$  space.  $\Gamma$  and  $\Gamma'$  are of a rather complex shape which need not concern us here, but they are mutually transformed into each other by the dynamical equations of motion for the inelastic collision if inverse collisions exist. Substituting the first of Eqs. (21) into Eq. (19) one obtains

$$Q(f, f) = n^2 \int \dots \int [f'_1 f'_2 \mathcal{J} - f_1 f_2] g I(\epsilon|\epsilon') d\epsilon' d\mathbf{e}' d\mathbf{c}_2 d\epsilon_2. \quad (22)$$

Integrating Eq. (20) over  $\Gamma$  on the left-hand side and  $\Gamma'$  on the right-hand side and using Eqs. (21) leads to a detailed balancing relation on  $I$ , if inverse collisions exist as

$$\epsilon_t \epsilon_1^{\zeta-1} \epsilon_2^{\zeta-1} I(\epsilon|\epsilon') = \epsilon_t' \epsilon_1'^{\zeta-1} \epsilon_2'^{\zeta-1} I(\epsilon'|\epsilon). \quad (23)$$

Note that except for the  $\mathcal{J}$  factor in the emission term, Eq. (22) is rather similar in form to the Wang-Chang-Uhlenbeck<sup>2</sup> equation for the semi-quantum mechanical gas.

### C. Model collision integral

Equation (18) with  $Q$  given by Eq. (22) was obtained by applying the information theory principle and then integrating over a constant  $\epsilon$  surface in  $\mathbf{q}$  space. While simpler than Eq. (15), its solution would still require treatment of the inelastic collision problem to enable determination of  $I$  through Eqs. (21). Instead of dealing with this case, we consider a simpler model by writing

$$I(\epsilon|\epsilon') = R(\epsilon|\epsilon') \sigma(\chi), \quad (24)$$

where  $\sigma$  is the cross section for some spherical scattering process and  $R(\epsilon|\epsilon') d\epsilon'$  is the probability of scattering into  $d\epsilon'$ ,  $R$  being the energy scattering kernel. Substituting Eq. (24) into Eq. (22) yields a model  $Q$  for which the monatomic (spherical) geometrical scattering properties in collisions are retained and the effects of polyatomicity as internal-translational energy exchange are described phenomenologically by a suitable choice of  $R$ . Generally,  $R$  will represent some stochastic model for the post collision  $\epsilon'$  distribution, for given  $\epsilon$ . The choice  $R(\epsilon|\epsilon') = \delta(\epsilon - \epsilon')$  will clearly recover the monatomic inelastic case.

For  $\sigma$ , we restrict our attention to inverse power molecules with the intermolecular potential  $V = a/r^\alpha$ , where  $r$  is the particle separation,  $\alpha$  is the potential exponent, and  $a$  is a constant. Since here  $\sigma g^{4/\alpha}$  is a function only of the impact parameter  $\omega = b(mg^2/2\alpha a)^{2/\alpha}$ ,  $b$  being the miss distance, then assuming  $\omega = \omega'$  is equivalent to  $\sigma' g'^{4/\alpha} = \sigma g^{4/\alpha}$ . Substituting this result and Eq. (24) into Eq. (23) leads to a detailed balancing or micro-reversibility condition on  $R(\epsilon|\epsilon')$

$$\epsilon_t^{\eta-1} \epsilon_1^{\zeta-1} \epsilon_2^{\zeta-1} R(\epsilon|\epsilon') = \epsilon_t'^{\eta-1} \epsilon_1'^{\zeta-1} \epsilon_2'^{\zeta-1} R(\epsilon'|\epsilon), \quad (25)$$

where  $\eta = 2 - 2/\alpha$ . In addition,  $R(\epsilon|\epsilon')$  must satisfy the following conditions:

(1) Energy conservation  $\epsilon_0 = \epsilon_1 + \epsilon_2 + \epsilon_t = \epsilon_1' + \epsilon_2' + \epsilon_t' = \epsilon_0'$  which insures energy and linear momentum conservation in collisions.

(2) Nonnegativity  $R \geq 0$  since  $R$  is a probability density.

(3) Normalization  $\int \int R(\epsilon|\epsilon') d\epsilon' = 1$  for all  $\epsilon$  since some  $\epsilon'$  must result from an encounter.

In the present theory  $R$  plays the same role and satisfies essentially the same properties as does the surface scattering kernel  $P(\mathbf{c}|\mathbf{c}')$  in gas-surface phenomenology.<sup>19</sup>

### D. s vector formulation

Here, we develop an alternative formulation which will allow consideration of exchange models for which direct construction of  $R(\epsilon|\epsilon')$  would be rather difficult. We introduce an  $l$  dimensional random "vector"  $\mathbf{s} = (s_1, s_2 \dots s_l)$  with probability density  $h(\mathbf{s}) = \prod_{i=1}^l h_i(s_i)$  such that  $\int \int h(\mathbf{s}) d\mathbf{s} = 1$ , where  $d\mathbf{s} = ds_1 ds_2 \dots ds_l$ . Forming the composite vectors  $(\epsilon, \mathbf{s})$  representing a pre-collision state and  $(\epsilon', \mathbf{s}')$ , a post collision state we assume the existence of a one-to-one mapping  $\mathcal{L}[(\epsilon, \mathbf{s})] = (\epsilon', \mathbf{s}')$  from unprimed to primed coordinates where  $\mathcal{L}$  is some operator which satisfies a self-invertable property

$$\mathcal{L}\{\mathcal{L}[(\epsilon, \mathbf{s})]\} = (\epsilon, \mathbf{s}). \quad (26)$$

Equation (26) means that two serial applications of  $\mathcal{L}$  recovers  $(\epsilon, \mathbf{s})$ . In addition, we require that  $\mathcal{L}$  must conserve energy  $\epsilon_1 + \epsilon_2 + \epsilon_t = \epsilon_1' + \epsilon_2' + \epsilon_t' = \epsilon_0$ .

We now seek conditions on  $h(\mathbf{s})$  for which we may write  $R(\epsilon|\epsilon')$ ,  $R(\epsilon'|\epsilon)$  as

$$R(\epsilon|\epsilon') d\epsilon' = \int \int_V h(\mathbf{s}) d\mathbf{s}, \quad R(\epsilon'|\epsilon) d\epsilon = \int \int_{V'} h(\mathbf{s}') d\mathbf{s}', \quad (27)$$

where  $V$  is the projection into  $\mathbf{s}$  space of a region  $\mathcal{R}$  of

$(\epsilon, \mathbf{s})$  space defined by a slice  $d\epsilon$  and bounded by hypersurfaces of constant  $\epsilon'_i, \epsilon'_i + d\epsilon'_i, i = 1, 2; \epsilon'_i, \epsilon'_i + d\epsilon'_i$  (defined through  $\mathcal{L}$ ).  $V'$  is the projection onto  $\mathbf{s}'$  space of  $\mathcal{R}'$  in  $(\epsilon', \mathbf{s}')$  space into which  $\mathcal{R}$  is mapped by  $\mathcal{L}$ , and we note that the interpretation of  $R$  as in Eqs. (27) requires that  $\mathcal{L}$  also maps  $\mathcal{R}' \rightarrow \mathcal{R}$ ; hence,  $\mathcal{L}$  must satisfy Eq. (26). Multiplying Eq. (25) by  $d\epsilon'$ , using Eqs. (27), and letting  $V \rightarrow ds, V' \rightarrow ds'$  yields the required condition on  $h(\mathbf{s})$  under  $\mathcal{L}$

$$\epsilon_1^{r-1} \epsilon_1^{r-1} \epsilon_2^{r-1} h(\mathbf{s}) d\mathbf{s} d\epsilon = \epsilon_1'^{r-1} \epsilon_1'^{r-1} \epsilon_2'^{r-1} h(\mathbf{s}') d\mathbf{s}' d\epsilon'. \quad (28)$$

Equations (26)–(28) simply mean that if we can find some  $\mathcal{L}$  satisfying Eq. (26) and energy conservation, and some  $h(\mathbf{s})$  satisfying Eq. (28) under  $\mathcal{L}$ , then  $R$  as in Eqs. (27) necessarily satisfies non-negativity, [since  $h(\mathbf{s}) \geq 0$ ], normalization [since  $\int h(\mathbf{s}) d\mathbf{s} = 1$ ] and detailed balancing, by virtue of Eq. (28). Substituting Eqs. (27) into Eq. (24), the result into Eq. (22), and extending the integration over  $\epsilon'$  to that over  $\mathbf{s}$  yields

$$Q(f, f) = n^2 \int \cdots \int [f_1' f_2' g - f_1 f_2] g \sigma d\mathbf{e}' h(\mathbf{s}) d\mathbf{s} d\mathbf{c}_2 d\epsilon_2 \quad (29)$$

which may be used in Eq. (18) to give our model kinetic equation.

Equation (29) may be viewed merely as an alternative to the  $R$  formulation. However, a more physical interpretation is possible. In the real case, the energy exchange is determined through the dynamical equations of motion with some (usually) asymmetric intermolecular potential. A logical consequence of these equations is the two-particle Liouville theorem, which allows  $Q(f, f)$  to be written as in Eq. (19). In the present model the exchange mechanism is modeled by some statistical process whereby  $\epsilon_1, \epsilon_2$ , and  $\epsilon_t$  may change their values by an amount determined by the properties of  $R(\epsilon|\epsilon')$  or equivalently by those of  $\mathcal{L}$  and  $h(\mathbf{s})$ . Since for the model  $\mathcal{L}$  will not be determined by dynamical considerations, it is necessary that  $h(\mathbf{s})$  satisfy Eq. (28) in imitation of the Liouville theorem, so that one may write our  $\mathbf{s}$  averaged  $Q(f, f)$  as in Eq. (29), retaining the Boltzmann-like form. In this sense  $\mathbf{s}$  plays the role of a kind of pseudo-internal coordinate set for the colliding pair and the self-invertible property of  $\mathcal{L}$  imitates the inverse collision property of some classical collision models.

For  $r$  separate energy modes with degrees of freedom  $\nu_i, i = 1 \dots r$  and  $f = f(\mathbf{c}, \epsilon_1, \epsilon_2 \dots \epsilon_r; \mathbf{x}, t)$ , Eq. (29) may be generalized as

$$Q(f, f) = n^2 \int \cdots \int \left( f_1' f_2' \prod_{i=1}^r g_i - f_1 f_2 \right) g \sigma d\mathbf{e}' h(\mathbf{s}) d\mathbf{s} d\mathbf{c}_2 \prod_{i=1}^r d\epsilon_{2,i} \quad (30)$$

together with a corresponding generalization of Eqs. (26) and (28).

### E. $H$ theorem and equilibrium

Identifying the  $H$  function with  $-s$  in Eq. (13) readily leads to an  $H$  theorem for our model  $Q$ . The detailed balancing condition Eq. (25) together with  $\omega = \omega'$  and the use of the monatomic scattering law is sufficient to de-

velop the appropriate integral transformations from which an  $H$  theorem may be obtained along standard lines.

The equilibrium  $f$  follows in the usual way from the fact that at equilibrium  $\ln(f/\epsilon^{r-1})$  must be a linear sum of the collisional invariants. If these are just the components of linear momentum and  $\epsilon_0$ , then applying the temperature, momentum, and normalization constraints yields

$$f_0(\mathbf{c}, \epsilon) = \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left[ -\frac{m}{2kT} (\mathbf{c} - \bar{\mathbf{c}})^2 \right] \frac{\epsilon^{\nu/2-1} \exp(-\epsilon/kT)}{\Gamma(\nu/2)(kT)^{\nu/2-1}}, \quad (31)$$

where  $T$  is the total temperature.

## III. SPECIAL MODELS OF THE EXCHANGE PROCESS

There remains the problem of obtaining special models of the exchange process. A special model is defined by specifying  $\mathcal{L}$  together with the form of  $h(\mathbf{s})$  or equivalently by defining  $R(\epsilon|\epsilon')$ . In either description, it will contain one or several disposable parameters which must be determined empirically or otherwise, specifying the extent to which  $\epsilon$  and  $\epsilon'$  are correlated through the statistical exchange process. The detailed balancing relations Eq. (25) or equivalently Eq. (28), together with the respective conservation conditions however, impose severe restrictions on admissible model forms. Borgnakke and Larsen<sup>14</sup> have presented a two-class elastic/inelastic exchange model analogous to the Maxwell law<sup>19</sup> in gas-surface theory, which satisfies these requirements. An extension<sup>15</sup> in which a constant fraction of the energy for each mode active during collision undergoes an elastic exchange process (restricted exchange) unfortunately does not properly satisfy either detailed balancing or the less restrictive integrated form of this condition. As an example of a class of exchange models conforming to the present theory, we now reformulate and generalize the restricted exchange scheme so as to overcome these difficulties.

### A. Partial exchange models: A particular case

We develop a particular case for  $r = 1$  in Eq. (30). Firstly, however, it is convenient to state a useful result from statistical distribution theory. Let  $x$  and  $z$  be independently distributed gamma ( $\gamma$ ) and beta ( $\beta$ ) variables, respectively, with joint distribution

$$dF(x, z) = \gamma(x|\mu_1 + \mu_2) \beta(z|\mu_1, \mu_2) dx dz, \quad (32)$$

where

$$\gamma(x|\mu) = [1/\Gamma(\mu)] x^{\mu-1} e^{-x}$$

is the normalized probability density for the  $\gamma$  distribution in  $x$ , with index (degrees of freedom)  $\mu > 0$ ,  $\beta(z|\mu_1, \mu_2)$  is the normalized density for the  $\beta$  distribution in  $z$  with indices  $\mu_1 > 0, \mu_2 > 0$ , defined by Eq. (6), and here  $F$  is the cumulative distribution function (in the statistical theory sense, not to be confused with the distribution function concept in the kinetic theory sense). Then, the transformation

$$x_1 = zx, \quad x_2 = (1-z)x \quad (33)$$

applied to Eq. (32) yields

$$dF(x_1, x_2) = \gamma \langle x_1 | \mu_1 \rangle \gamma \langle x_2 | \mu_2 \rangle dx_1 dx_2. \quad (34)$$

That is, a  $\gamma$  variable  $x$  with index  $\mu = \mu_1 + \mu_2$  can be decomposed into independent  $\gamma$  variables  $x_1, x_2$  (such that  $x = x_1 + x_2$ ) with indices  $\mu_1, \mu_2$  through Eqs. (33) and the introduction of the  $\beta$  variable  $z$ . Conversely, the sum of two independent  $\gamma$  variables with indices  $\mu_1, \mu_2$  is also a  $\gamma$  variable with index  $\mu_1 + \mu_2$ . From Eqs. (32) and (34) it follows that the Jacobean of Eqs. (33) must satisfy

$$\frac{\partial(x_1, x_2)}{\partial(x, z)} = \frac{\gamma \langle x | \mu_1 + \mu_2 \rangle \beta \langle z | \mu_1, \mu_2 \rangle}{\gamma \langle x_1 | \mu_1 \rangle \gamma \langle x_2 | \mu_2 \rangle}. \quad (35)$$

We now develop a "partial exchange" model based on Eqs. (32)–(35). For brevity, in what follows we use  $\{x; \gamma \langle x | \mu \rangle\}$  to denote "the random variable  $x$  with probability density  $\gamma \langle x | \mu \rangle$ " etc. Writing  $\xi = \epsilon/kT'$ , where  $T'$  is any reference temperature and multiplying Eq. (28) on both sides by the constant (for collisions)  $\exp(-\xi_1 - \xi_2 - \xi_t)$ , the detailed balancing condition becomes

$$\gamma \langle \xi_1' | \xi \rangle \gamma \langle \xi_2' | \xi \rangle \gamma \langle \xi_t' | \eta \rangle h(\mathbf{s}') d\xi' d\mathbf{s}' \\ = \gamma \langle \xi_1 | \xi \rangle \gamma \langle \xi_2 | \xi \rangle \gamma \langle \xi_t | \eta \rangle h(\mathbf{s}) d\xi d\mathbf{s}, \quad (36)$$

where  $\xi_t = mg^2/4kT'$ ,  $\xi = (\xi_1, \xi_2, \xi_t)$ , and where for present purposes we regard  $\xi_1, \xi_2, \xi_t$  as  $\gamma$  variables with densities implied in Eq. (36). We now make a particular choice for  $h(\mathbf{s})$ , reasons for which will become clear in the development, as

$$h(\mathbf{s}) = \left[ \prod_{j=1}^2 \beta \langle s_j | \phi \xi, (1-\phi) \xi \rangle \right] \beta \langle s_3 | \psi \eta, (1-\psi) \eta \rangle \\ \times \beta \langle s_4 | \phi \xi, \phi \xi \rangle \beta \langle s_5 | 2\phi \xi, \psi \eta \rangle, \quad (37)$$

where here  $\mathbf{s} = (s_1, s_2, s_3, s_4, s_5)$  and where  $1 > \phi(\xi_0, \omega) > 0$ ,  $1 > \psi(\xi_0, \omega) > 0$  are arbitrary functions (model parameters) of  $\xi_0 = \xi_1 + \xi_2 + \xi_t = \xi'_0$  and  $\omega$ .

Substituting Eq. (37) into Eq. (36) yields, on the right-hand side factors of the form  $\gamma \langle \xi_i | \eta \rangle \beta \langle s_3 | \psi \eta, (1-\psi) \eta \rangle$  together with like factors for the  $\xi_1, \xi_2$  terms. Identifying these factors with the right-hand side of Eq. (32) and utilizing the properties of the  $\gamma$  and  $\beta$  distributions discussed here, the transformation, modeled on Eqs. (33)

$$e_i' = s_3 \xi_i, \quad e_i' = s_4 \xi_i, \quad (38a) \\ e_i'' = (1-s_3) \xi_i, \quad e_i'' = (1-s_4) \xi_i, \quad i=1, 2,$$

decomposes  $\{\xi_i; \gamma \langle \xi_i | \eta \rangle\}$  into the "partial energies"  $\{e_i'; \gamma \langle e_i' | \psi \eta \rangle\}$  and  $\{e_i''; \gamma \langle e_i'' | (1-\psi) \eta \rangle\}$  and also  $\{\xi_i; \gamma \langle \xi_i | \xi \rangle\}$  into partial energies  $\{e_i'; \gamma \langle e_i' | \phi \xi \rangle\}$  and  $\{e_i''; \gamma \langle e_i'' | (1-\phi) \xi \rangle\}$ ,  $i=1, 2$ , respectively.

Following Ref. 15 and regarding  $e_i'$  as the translational energy available for exchange during collision and  $e_i''$  as inactive together with a similar interpretation of the  $e_i', e_i''$ , then the transformations [inverse of Eqs. (33)]

$$e_i' = e_i' + e_i'', \quad e_i' = e_i' + e_i', \quad (38b) \\ s_i' = e_i' / (e_i' + e_i''), \quad s_i' = e_i' / (e_i' + e_i'),$$

combines the active partial energies into  $\{e_a'; \gamma \langle e_a' | \psi \eta + 2\phi \xi \rangle\}$  and generates the new quantities  $\{s_a'; \beta \langle s_a' | \phi \xi, \phi \xi \rangle\}$

and  $\{s_i'; \beta \langle s_i' | 2\phi \xi, \psi \eta \rangle\}$ . Utilizing the remaining  $\beta \langle s_4 | \phi \xi, \phi \xi \rangle$ ,  $\beta \langle s_5 | 2\phi \xi, \psi \eta \rangle$  in Eq. (37), then

$$e_i''' = s_5 e_a', \quad e_i''' = s_4 e_i''' \quad (38c) \\ e_i''' = (1-s_5) e_a', \quad e_i''' = (1-s_4) e_i'''$$

decomposes  $e_a'$  into post collision partial energies  $\{e_i'''; \gamma \langle e_i''' | \psi \eta \rangle\}$  and  $\{e_i'''; \gamma \langle e_i''' | \phi \xi \rangle\}$ ,  $i=1, 2$  respectively. Finally, adding these to their respective inactive partials through

$$\xi_i' = e_i'' + e_i''', \quad \xi_i' = e_i'' + e_i''' \\ s_i' = e_i''' / (e_i'' + e_i'''), \quad s_i' = e_i''' / (e_i'' + e_i'''), \quad (38d) \\ i=1, 2$$

generates the post collision energies together with the new quantities  $\{s_i'; \beta \langle s_i' | \phi \xi, (1-\phi) \xi \rangle\}$ ,  $i=1, 2$  and  $\{s_i'; \beta \langle s_i' | \psi \eta, (1-\psi) \eta \rangle\}$ . Eliminating intermediate quantities in Eqs. (38) and multiplying by  $kT'$  we obtain an explicit  $L$  as a simple algebraic transformation

$$\epsilon_1' = (1-s_1) \epsilon_1 + s_4 s_5 \epsilon_a, \quad \epsilon_2' = (1-s_2) \epsilon_2 + (1-s_4) s_5 \epsilon_a, \quad (39a) \\ \epsilon_t' = (1-s_3) \epsilon_t + (1-s_5) \epsilon_a,$$

$$s_1' = s_4 s_5 \epsilon_a / \epsilon_1', \quad s_2' = (1-s_4) s_5 \epsilon_a / \epsilon_2', \\ s_3' = (1-s_5) \epsilon_a / \epsilon_t', \quad s_4' = s_1 \epsilon_1 / (s_1 \epsilon_1 + s_2 \epsilon_2), \quad (39b) \\ s_5' = (s_1 \epsilon_1 + s_2 \epsilon_2) / \epsilon_a,$$

where  $\epsilon_a = s_1 \epsilon_1 + s_2 \epsilon_2 + s_3 \epsilon_t = s_1' \epsilon_1' + s_2' \epsilon_2' + s_3' \epsilon_t'$ .

Using the appropriate form of Eq. (35) for each of the ten transformations in Eqs. (38), and the chain rule for Jacobians, it may be shown that Eq. (36) is satisfied by Eqs. (39) with  $h(\mathbf{s})$ ,  $h(\mathbf{s}')$  given by Eq. (37). Manipulation of Eqs. (39) shows that energy conservation and Eq. (26) are satisfied (this should be clear from the method of construction), and hence, the model is consistent with  $Q(f, f)$  given by Eq. (29). This model is similar to that of Ref. 15 except that in the latter case, active partials were taken as constant fractions of  $\epsilon_t$  and  $\epsilon_t = \epsilon_1 + \epsilon_2$ , respectively. This led to restrictions on  $\epsilon_1'$ ,  $\epsilon_2'$ , and  $\epsilon_t'$ , whereas in our case these quantities all lie in  $(0, \epsilon_0)$ , but for small  $\phi, \psi$ , each is narrowly distributed about  $\epsilon_1, \epsilon_2$ , and  $\epsilon_t$ , respectively. The essential idea behind the models is that while active partial energies undergo a completely elastic exchange process in which pre- and post-collision values are uncorrelated [Eqs. (38b)–(38c)], the inactive partials behave inelastically thus retaining some correlation for the overall participating energies. The choice of Eqs. (37) for  $h(\mathbf{s})$  facilitates modeling of this process such that the required conditions are satisfied, using Eqs. (32)–(34).

The functional parameters  $\psi$  and  $\epsilon$  may be shown to be respectively equal to the  $\mathbf{s}$  averaged fraction of  $\epsilon_t$  and  $\epsilon_1, \epsilon_2$  available for exchange per collision. They are thus a measure of the ease with which exchange takes place for particular  $\epsilon_0$  and  $\omega$ . From Eqs. (37) and (39) it follows that the limit  $\phi \rightarrow 0, \psi \rightarrow 0$  leads to the inelastic (monatomic) case while  $\phi \rightarrow 1, \psi \rightarrow 1$  yields the perfectly elastic model of Ref. 14. The limit  $\psi \rightarrow 0$  yields a model which is inelastic for translational-rotational exchange, but allows partial exchange of order  $\phi$  between particle internal energies. Here, both  $\epsilon_t = \epsilon_1 + \epsilon_2$  and  $\epsilon_t$  are col-

lisional invariants. Hence, in homogeneous relaxation the velocity and internal energy distributions will approach the translational and internal distribution function factors of Eq. (31) separately in order one, and  $1/\phi$  collision times, respectively. At equilibrium separate translational and internal temperatures will be maintained.

Further particular cases of partial exchange models may be readily constructed; for example, the generalization of Eqs. (37) and (39) to  $r$  internal energy modes each with separate  $\psi_i$ ,  $\phi_i$ ,  $i=1 \dots r$ . The cross section  $R(\epsilon|\epsilon')$  for these models including the present case can be formally obtained using Eqs. (27), but the result is usually very complicated and not useful in practice. On the other hand, Eqs. (37) and (39a) are simple and may be readily used in Monte-Carlo or other applications. Note that while the  $s'$  information in Eqs. (39b) is not required in practice, it must be considered here to establish detailed balancing.

## B. Choice of disposable parameters: Transport properties

Here, we give results for the transport coefficients of a gas conforming to the present partial exchange model. These may be used in choosing  $\phi(\xi_0, \omega)$  and  $\psi(\xi_0, \omega)$  for some particular application. Hirschfelder *et al.*<sup>2</sup> give explicit transport formulae for the quasi-quantum mechanical gas, obtained from a Chapman-Enskog solution to the Wang-Chang-Uhlenbeck equation. Expressions valid for the present theory may be derived by replacing the discrete quantum internal energy levels by the continuous set given in Eq. (31), and also the internal state transition probabilities by our equivalent  $h(\mathbf{s})d\mathbf{s}$  or  $R(\epsilon|\epsilon')d\epsilon'$ . For example, the relaxation time  $\tau$  for inverse power molecules becomes

$$\tau^{-1} = \frac{2n}{9\nu\Gamma^2(\nu/2)} \left(\frac{kT}{m}\right)^{1/2} \left(\frac{\alpha a}{2kT}\right)^{2/\alpha} \int \dots \int \xi_1^{\nu/2-1} \xi_2^{\nu/2-1} \xi_t^{1-2/\alpha} \times \exp(-\xi_1 - \xi_2 - \xi_t) (\Delta\xi)^2 \omega d\omega d\theta h(\mathbf{s}) d\mathbf{s} d\xi_1 d\xi_2 d\xi_t, \quad (40)$$

where  $\xi_i = \epsilon_i/kT$ ,  $i=1, 2$ ,  $\xi_t = \epsilon_t/kT$ ,  $\Delta\xi = \xi'_1 + \xi'_2 - \xi_1 - \xi_2$ ,  $T$  is the equilibrium temperature and where we have transformed  $\sigma d\theta'$  to impact parameter equivalent  $\omega d\omega d\theta$ . Corresponding formulae for other transport coefficients may readily be obtained in like manner.

For  $r=1$  and the exchange model of Sec. IIIA we give explicit results for the internal relaxation number  $Z = \tau\tau_c^{-1}$ , where the mean collision time  $\tau_c$  is

$$\tau_c = \pi\mu_0(T)/4nkT \quad (41)$$

and

$$\mu_0(T) = \frac{5(mkT/\pi)^{1/2}(2kT/\alpha a)^{2/\alpha}}{8A_2(\alpha)\Gamma(4-2/\alpha)}$$

is the zeroth order viscosity for inverse power molecules, and also for the viscosity  $\mu(T)$  and heat conductivity  $\lambda(T)$ . These were obtained by substituting  $\Delta\xi$  from Eqs. (39a) and  $h(\mathbf{s})$  from Eq. (37) into the appropriate transport integrals and performing 8 of the 10 integrations analytically in each case. Expressions for  $Z$  and  $\mu$  are exact while that for  $\lambda$  requires the approxi-

mation  $\xi_t^{1/2}(\xi_2 - \xi_1) \approx \xi_t'^{1/2}(\xi_2' - \xi_1')$  and is valid only for  $\max|\phi| < 1$ ,  $\max|\psi| < 1$ , and only to first order in these quantities. The final results are

$$Z^{-1} = \frac{5\pi}{4(3-2/\alpha)A_2(\alpha)} H_0, \quad (42a)$$

$$\left(\frac{\mu}{\mu_0}\right)^{-1} = 1 + \frac{\nu}{(2-2/\alpha)A_2(\alpha)} H_1, \quad (42b)$$

$$\lambda = \lambda_1 + \lambda_2, \quad (42c)$$

where

$$\lambda_1 = \frac{75}{32A_2(\alpha)\Gamma(4-2/\alpha)} \left(\frac{k^3T}{\pi m}\right)^{1/2} \left(\frac{2kT}{\alpha a}\right)^{2/\alpha} \times \left\{ 1 + \nu \left[ \frac{H_0}{2A_1(\alpha)} - \frac{H_2}{(3-2/\alpha)A_2(\alpha)} \right] \right\},$$

$$\lambda_2 = \frac{9\nu}{48A_1(\alpha)\Gamma(3-2/\alpha)} \left(\frac{k^3T}{\pi m}\right)^{1/2} \left(\frac{2kT}{\alpha a}\right)^{2/\alpha} \times \left\{ 1 + H_0 \left[ \frac{25}{4(3-2/\alpha)A_2(\alpha)} - \frac{3}{2A_1(\alpha)} \right] \right\},$$

and where

$$A_e(\alpha) = \int_0^\infty (1 - \cos^e \chi) \omega d\omega; \quad H_0 = \int_0^\infty K(\omega) \omega d\omega$$

$$H_1 = \int_0^\infty K(\omega) \left(\frac{2}{3} - \sin^2 \chi\right) \omega d\omega; \quad H_2 = \int_0^\infty K(\omega) \left(\frac{11}{4} - \sin^2 \chi\right) \omega d\omega$$

with

$$K(\omega) = \frac{1}{\Gamma(\nu+4-2/\alpha)} \int_0^\infty \frac{\phi\psi}{[\phi\nu+\psi(2-2/\alpha)]} \xi_0^{\nu+3-2/\alpha} e^{-\xi_0} d\xi_0,$$

where  $\xi_0 = \xi_1 + \xi_2 + \xi_t$  and  $\chi = \chi(\omega)$  is the deflection angle.

For  $\alpha \rightarrow \infty$ , i.e., hard spheres, and the choice  $\psi = \phi$ ,  $\omega < 1$ ;  $\psi = \phi = 0$ ,  $\omega > 1$ , Eqs. (42) reduce to

$$Z = \frac{8(2+\nu)}{5\pi} \frac{1}{\phi_0}, \quad (43a)$$

$$\mu = \mu_0, \quad (43b)$$

$$\lambda_1 = \frac{75}{64d^2} \left(\frac{k^3T}{\pi m}\right)^{1/2} \left(1 - \frac{13\nu}{24(2+\nu)} \phi_0\right), \quad (43c)$$

$$\lambda_2 = \frac{9\nu}{48d^2} \left(\frac{k^3T}{\pi m}\right)^{1/2} \left(1 + \frac{13}{8(2+\nu)} \phi_0\right), \quad (43d)$$

where  $d$  is the hard sphere diameter. Equation (43a) shows that  $Z$  is inversely proportional to  $\phi$  as might be expected while the viscosity correction in Eq. (43b) vanishes essentially due to the inelastic isotropy implied in the choice for  $\phi(\omega)$  and  $\psi(\omega)$ . Note that Eqs. (43c) and (43d) agree with the results of an approximate transport theory due to Mason and Monchick (Ref. 3, p. 326 and Ref. 21).

## C. Behavior in simulation

The present partial exchange model was tested in Bird's direct simulation Monte-Carlo scheme. The hard sphere gas with  $\nu=2$  was employed with  $\phi, \psi$  being chosen as outlined herein, to simulate the homogeneous relaxation problem. The simulation was initialized by choosing velocity vectors distributed on the unit sphere ( $c_x^2 + c_y^2 + c_z^2$ )/ $2RT = \frac{5}{2}$ , in  $c_x - c_y - c_z$  space, for each of  $N$

TABLE I. Direct simulation method CDC-6400 computing times per 1000 collisions for models tested.

Model	$\phi=0.5$	$\phi=0.2$	$\phi=0.1$
Monatomic	1.27	1.27	1.27
Ref. 15, $\nu=2$	2.50	2.12	2.04
Present, $\nu=2$	5.02	4.46	4.17

= 2000 sample particles, where  $T$  is the equilibrium temperature for  $\nu=2$ . With  $\epsilon=0$  initially for each particle this corresponds to initial translational and rotational temperatures of  $T_t = \frac{5}{3}T$  and  $T_r=0$ , respectively. The calculation proceeds by computing collisions according to the scheme described in Ref. 4 and in the present application, a standard method<sup>22</sup> was employed for generating the beta variables required for the exchange calculation. Time was nondimensionalized as  $\hat{t}=t/\tau_c$  where for hard spheres  $\tau_c$  is given by Eq. (41) with  $\mu_0 = 5(\pi mkT)^{1/2}/16\pi d^2$ .

Figure 1 shows the ratio of temperature difference to initial difference  $(T_t - T_r)/(T_t - T_r)_0$  vs  $\hat{t}/Z$  for several values of  $\phi_0$ , where  $Z$  is given by Eq. (43a). Also shown are similar results for the restricted exchange model, and the theoretical result

$$(T_t - T_r)/(T_t - T_r)_0 = \exp[-(3+\nu)\hat{t}/3Z] \quad (44)$$

based on the equations of change for  $T_t$ ,  $T_r$  derived from the Chapman-Enskog solution. The relaxation behavior of the models are similar with the effective  $Z$  being approximately constant during relaxation and generally less than the theoretical value (the exception being  $\phi_0=0.5$  for the present model). The discrepancies can be largely attributed to the fact that the Chapman-Enskog theory is valid for only small departures from equilibrium. There are, however, small but discernable differences in the large time internal energy distributions for the two models shown in Fig. 2 where

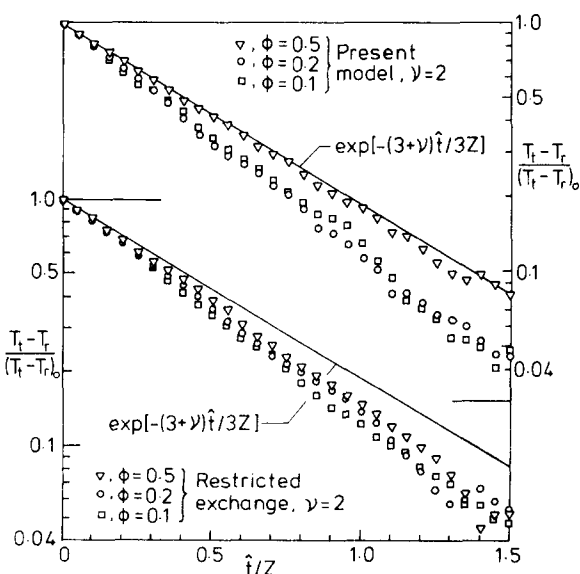


FIG. 1. Relaxation behavior for restricted exchange model and present modified version.

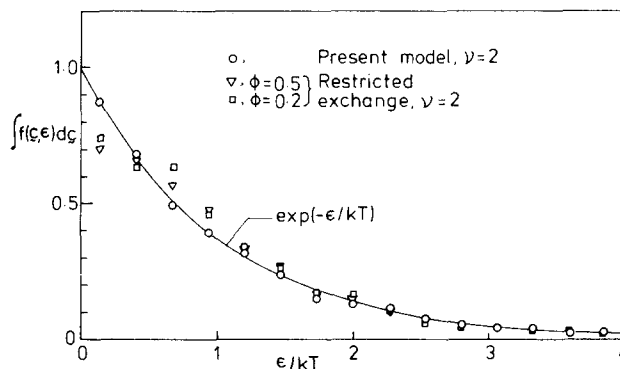


FIG. 2. Internal energy distribution at equilibrium for restricted exchange model and modified version.

the  $H$  theorem for the present model guarantees that the Boltzmann distribution will be obtained at equilibrium. Here, we have chosen fixed  $\phi, \psi$  corresponding to constant  $Z$ ; however, the model has the flexibility to allow approximate matching of any desired temperature variation of  $Z$  say, through Eqs. (42).

Table I shows approximate CDC-6400 execution times per 1000 collisions for the models tested compared with times for a monatomic gas simulation. The present model requires five beta variables per collision calculation compared with two per collision for the restricted exchange model and therefore is the slower of the two. In some cases, then, where this latter model has been properly tested, it is probably to be preferred to the present modified version. For more complex problems than have been treated here, say for a gas with several internal energy modes, the present model is perhaps superior. Note that computing times for these phenomenological models are one to two orders of magnitude smaller than currently reported times for the semi-classical models of Refs. 12 and 13.

#### IV. CONCLUDING REMARKS

Phenomenological models of the complex energy exchange processes in inelastic collisions of polyatomic molecules appear to be an acceptable alternative to the classical or semi-classical approach. We have presented a theory for certain classes of such models and have shown how one recently proposed special model describing a particular mode of exchange may be reconstructed within its general framework. Other special models may be readily constructed. Using methods proposed by Cercignani<sup>23</sup> for the construction of  $P(c|c')$  in gas-surface theory, it is possible to obtain an apparently unlimited number of forms for the differential scattering cross section  $R(\epsilon|\epsilon')$ , all of which satisfy the required conditions of energy conservation, microreversibility, nonnegativity, and normalization. However, the physical interpretation of models constructed in this manner is not always straightforward and their usefulness is therefore rather difficult to access. It is not clear whether the partial exchange models are the only class of models that can be constructed within the  $s, h(s)$  formulation. This seems unlikely, however, and further investigation will undoubtedly produce other cases.

Although we have presently considered only a single species chemically inert gas, the extension of the present theory to a chemically inert gas mixture with a different internal structure for each species is quite straightforward. The further extension, particularly of the partial exchange models to a nonequilibrium chemically reacting system would be an interesting area for future investigation.

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